

Differential Accumulation of Polychlorinated Biphenyl Congeners in the Aquatic Food Web at the Kalamazoo River Superfund Site, Michigan

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A series of field studies were conducted to gain a better understanding of the bioaccumulation and dynamics of polychlorinated biphenyl (PCB) congeners in the aquatic food web of the Kalamazoo River flood plain. Representative species of passerine birds, mammals, fish, aquatic plants, invertebrates, and colocated sediments were collected from areas located within submerged portions of the former Trowbridge impoundment and also from areas located at an upstream reference location. In most matrixes, total concentrations of PCBs were significantly greater in the downstream study area compared to the upstream reference location. Patterns of PCB congeners varied among trophic levels due to selective bioaccumulation of more chlorinated congeners in upper trophic level organisms. There were no statistically significant differences in total PCB concentrations among sampling grids within either site or temporally among three sampling seasons between May and September. The greatest total PCB concentrations were detected in adult tree swallows (mean = 8.7 mg/kg wet weight (ww)) and fish (mean = 4.4 mg/kg ww) collected from the former Trowbridge impoundment. Concentrations of total 2,3,7,8-tetrachlorodibenzo-*p*-

dioxin equivalents (TEQs) were greatest in egg, nestling, and adult tree swallows collected from the former Trowbridge impoundment. There was not a significant correlation between concentrations of total PCBs and TEQs at either site in the mammalian or avian food webs. The relative potency of the mixture of PCBs, expressed as the ratio of TEQs to total PCBs, increased with trophic position in the avian and mammalian aquatic food webs located within the former Trowbridge impoundment.

Introduction

In 1990, approximately 80 miles of the Kalamazoo River was designated a Superfund site and termed the Kalamazoo River Area of Concern (KRAOC). The primary contaminants of potential ecological concern (COPECs) at this site are polychlorinated biphenyls (PCBs), of which there are 209 possible PCB congeners, varying in the number and positions of chlorine substitution. The release of PCBs in the KRAOC resulted from PCB-contaminated waste discharged from the recycling and processing of carbonless copy paper (1). During the period from 1957 to 1971, the ink solvent used in carbonless copy paper contained mixtures of PCBs, primarily Aroclor 1242 (2).

Previously, site-specific PCB data from samples collected from the KRAOC have been quantified as Aroclors 1016, 1242, 1248, 1254, and/or 1260 depending on what peaks were monitored and what standards were used (3). However, due to environmental weathering and other biological processes including selective volatilization, degradation, accumulation, sorption, and metabolism, the relative concentrations of PCB congeners in a mixture or matrix change as a function of time and do not match the original Aroclor formulation. The weathering of PCB congeners as they pass through the various compartments of the food web results in patterns of relative congener concentrations in biota that are variable and significantly different from that of the original Aroclor mixture (4). Therefore, the analytical methodologies used in these investigations do not quantify "Aroclors", but rather concentrations of individual congeners are used to calculate total PCB concentrations and compare patterns. Limitations associated with Aroclor-based determination of PCBs in environmental samples have long been recognized (5–10). Congener-specific analysis, including coplanar PCB congeners, is generally thought to correlate better with toxicity than measures of total PCBs as quantified by Aroclor analysis (11).

This study evaluated the spatial differences in absolute concentrations of total PCBs in sediments, aquatic plants, and biota collected within and between various sampling locations, including an upstream reference site and a downstream study site within the KRAOC. An additional objective of this study was to measure concentrations of total PCBs in sediments, plants, and invertebrates collected during distinct time periods to evaluate seasonal differences in PCB concentrations. In addition, concentrations of total PCBs were measured in field-collected samples such that site-specific biota–sediment accumulation factors (BSAFs) and biomagnification factors (BMFs) could be evaluated among various trophic positions. Concentrations of individual PCB congeners and patterns of relative concentrations among trophic levels were contrasted to gain a better understanding of the chemodynamics of PCBs in this aquatic food web. Finally, the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) equivalent concentrations (TEQs) and relative potencies of

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the PCB mixtures were determined for various trophic positions within the aquatic food web.

Experimental Section

Study Area Locations. This food web analysis study was focused on two general areas along the Kalamazoo River, an area located upstream of historical point sources of PCBs and an area located within the KRAOC. Within the KRAOC, the former Trowbridge impoundment was selected as a study site since it is the largest of the three former impoundments on the Kalamazoo River, and it has the greatest surficial mean concentration of PCBs in soils. Within the former Trowbridge impoundment, four sampling grids were established for aquatic sample collections. These adjacent sampling grids at the KRAOC were separated by 0.3–1.0 km. Upstream of the KRAOC, the Fort Custer State Recreation Area (FC) was selected as a reference site for this study. FC is located 30 miles upstream of the former Trowbridge impoundment and is relatively uncontaminated with PCBs. Two sampling grids were established within FC for sample collection. These sampling grids within FC were located 2.5 km apart.

Sample Collection. On the basis of previous PCB sediment data from the KRAOC, sediment and invertebrate biota were collected from sampling grids based on a gradient of potential exposure. Exact sampling locations within sampling grids were randomly determined with the use of random number tables. Sediments, aquatic plants, and benthic invertebrates were collected simultaneously using a PONAR grab sampler from sampling grids. Collected sediment samples were pooled for a given transect and placed into clean, labeled buckets. Aquatic plants were removed from the sediment grab sample, rinsed with distilled water, and separated by species. Each plant species was weighed and combined into a pooled composite for each sampling location. Sediment-associated benthic macroinvertebrates were collected by removing and sieving the top fraction of collected sediment samples. Collection of benthic macroinvertebrates continued until at least 3 g of biomass was obtained from each sampling location. Crayfish were collected using a baited minnow trap and seining. Collected crayfish were weighed and transferred to chemically clean glass jars. Aquatic emergent insects were sampled during the first 3 h after sunset, since the prevalent aquatic emergent insect species (diptera (chironomidae), ephemeroptera (mayflies), and trichoptera (caddisflies)) exhibit the greatest flight activity at this time. Aquatic emergent insects were sampled by high-pressure vapor lamp, aerial and sweep nets, or by hand-picking. All collected insects were classified, and composites were made for analysis on an order-specific basis.

To evaluate the accumulation of PCB congeners into upper trophic levels of the aquatic food web, tree swallows (*Tachycineta bicolor*), mink (*Mustela vison*), muskrats (*Onychomys leucogaster*), and several species of fish were also collected from the Kalamazoo River. Fish were collected from both the KRAOC and FC by electrofishing, gill-netting, or trap-netting. Tree swallow eggs, nestlings, and adults were collected during nest box studies at the FC and KRAOC areas. All addled eggs and one fresh (viable) egg/nest box were collected. Nestling tree swallows were randomly selected for sampling. Chicks were removed from the nest, weighed, and euthanized by cervical dislocation. Tree swallow adults were collected opportunistically post fledging of nestlings. Detailed methods of tree swallow collection procedures are discussed elsewhere (12, 13). Mink and muskrat specimens were collected from traps along the Kalamazoo River. Detailed methodologies for these collections are discussed elsewhere (14). The extent of the river sediment and flood plain habitat that is contaminated with PCBs is greater than the extent of the foraging range of upper trophic level organisms con-

sidered in this study with the exception of tree swallows, which exhibit migratory behavior.

Sampling Events. Carp (*Cyprinus carpio*), suckers (*Catostomus commersoni*, *Hypentelium nigricans*, and *Moxostoma erythrurum*), and smallmouth bass (*Micropterus dolomieu*) were collected at the Trowbridge impoundment during the fall of 1999. Sediments, aquatic plants, benthic invertebrates, crayfish, aquatic emergent insects, and tree swallow eggs, nestlings, and adults were collected during 2000, 2001, and 2002, with most samples being collected during 2000 and 2001. To address seasonal variations in total PCB concentrations, sediments, aquatic plants, benthic invertebrates, crayfish, and aquatic emergent insects were collected during distinct sampling periods during the 2000 spring, summer, and autumn sampling seasons. Period 1 collections of sediments, plants, and invertebrates took place from May 22 to June 21. Period 2 took place from July 17 to Aug 16, and period 3 collections started on Aug 24 and ended on Sept 19.

Analytical Methodology. From the time of collection until extraction, samples, apart from tree swallow eggs, were kept frozen at -20°C . Tissue homogenization, extraction, and chemical analysis followed procedures that were similar to those reported elsewhere (15). Tissues were homogenized with anhydrous sodium sulfate and added to a Soxhlet extractor. Surrogate standards (PCBs 204 and 30) were added to all samples, blanks, and matrix spikes before extraction. The matrix spike solution (containing a mixture of PCB congeners) was added to the matrix spike samples and matrix blank samples. A sodium sulfate laboratory blank, matrix spike, matrix spike duplicate, and standard reference material were run with each extraction batch of 20 samples. Surrogate recoveries were determined to be acceptable within the range of 65–135%. No corrections were made to concentrations based on surrogate recoveries; however, if the limits were not met for the mass spectrometry mass-selective detector, then all of the samples in the analytical batch were re-extracted. Sample results were flagged if PCB concentrations in the sample were less than 3 times the value detected in the blank. Samples were Soxhlet-extracted for 18 h in a 3:1 mixture of dichloromethane/hexane. The extracts were then rotary/nitrogen evaporated to a final volume of 11 mL. After concentration, 1 mL of the extract was removed for gravimetric determination of lipid content. The remaining 10 mL of the extract was passed through a sulfuric acid silica gel column to remove lipids. Additional sulfuric acid cleanup was necessary if the extract eluting from the acidic silica gel column still contained significant amounts of organic material. The final extract was concentrated to 1 mL. PCB congeners were quantified by use of a gas chromatograph (Perkin-Elmer AutoSystem or Hewlett-Packard 5890 SII) equipped with a ^{63}Ni electron capture detector (GC-ECD) (15). Solutions containing 98 individual PCB congeners with known composition and content were used as standards. Congeners were identified by comparing sample peak retention times to those of the known standards, and concentrations of each congener were determined by comparing the peak area to that of the appropriate peak in the standard curve. All analytical sequences included an initial five-point calibration curve and calibration curve check standards after every sample injection. Sample analysis was performed only if the initial calibration was linear and if the continuing calibration check standard was within $\pm 25\%$ of the original midpoint value. If analytical results were outside of the linear range, then the sample was diluted and reanalyzed. A conservative estimate of the method detection limit (MDL) for individual congeners is 1 ppt. This MDL is based on the injection volume of 1 μL , the excellent signal-to-noise ratio of a 25 ppt standard, and the mass of sample extracted.

Non-ortho-substituted (coplanar) PCB congeners 77, 81, 126, and 169 were separated from coeluting congeners and interferences by cleanup on a carbon-impregnated silica gel column (16). Extracts were analyzed by gas chromatography/mass spectrometry (GC-MS) on a Hewlett-Packard 5890 series II gas chromatograph equipped with a HP 5972 series mass-selective detector. Non-ortho-substituted PCB congeners were detected and confirmed by selected ion monitoring of the two largest ions of the molecular cluster using isotope dilution.

Calculation of BSAFs and BMFs. Biota-sediment accumulation factors (BSAFs) were calculated by dividing the geometric mean concentrations of PCBs in biota (using lipid-normalized data) by the geometric mean concentrations of PCBs in sediments (using organic-carbon-normalized data). Similarly, biomagnification factors (BMFs) were calculated by dividing the geometric mean concentrations of PCBs in upper trophic level organisms (using lipid-normalized data) by the geometric mean concentrations of PCBs in lower trophic level organisms (using lipid-normalized data).

Calculation of TEQ Concentrations. The relative toxic potencies of PCB mixtures measured in sediments and biota were assessed by calculating 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) equivalent concentrations (TEQs). For each sample, TEQs were calculated by summing the products of coplanar (77, 81, 126, and 169) and mono-ortho (105, 114, 118, 123, 156, 157, 167, and 189) PCB congener concentrations and their toxic equivalency factors (TEFs). The 1998 World Health Organization (WHO) TEF_{WHO} values (17) were used in these calculations for coplanar PCB congeners and mono-ortho PCB congeners. Due to the differing sensitivities of mammals, birds, and fish toward PCBs and other dioxin-like chemicals, three sets of TEF_{WHO} values have been developed for TEQ calculations that apply to mammalian, avian, and fish receptor species (17). For the TEQs presented here, TEF_{WHO} mammalian values were used for the mammalian food web, and TEF_{WHO} avian values were used for the avian food web. In this study, when mono-ortho congeners coeluted with other PCB congeners, the total concentration for that coeluting pair was considered to be entirely due to the mono-ortho congener. Thus, for a sample with coeluting congeners, the PCB TEQ_{WHO} concentration was overestimated. For PCB congeners that were present at concentrations less than the MDL, one-half of the MDL was assigned as a proxy concentration for that congener, and total TEQ concentrations were calculated using this data set.

Statistical Analysis. The Kolmogorov-Smirnov one-sample test with Lilliefors' transformation was used to assess whether data sets were normally distributed. When data were normally distributed, analysis of variance (ANOVA) followed by Tukey's honestly significant difference (HSD) was used to test for significant differences among data sets. When data sets were not normally distributed, the nonparametric Kruskal-Wallis test was used to test for differences among data sets. When comparing total PCBs between KRAOC and FC locations, the two-group t-test or the Mann-Whitney U-test was used if the data was normally distributed or nonnormally distributed, respectively (18). The criterion for significance that was used in all statistical tests was $p < 0.05$.

Results and Discussion

Spatial Variability in Total PCB Concentrations: Within the KRAOC and FC. To assess spatial variability within the KRAOC and FC, concentrations of total PCBs from different sampling grids were compared within these two locations. Concentrations of total PCBs in sediments, aquatic plants, benthic invertebrates, aquatic emergent insects, and crayfish were not significantly different between the two sampling grids at FC. At the KRAOC, there were no observed trends in total PCB concentrations in aquatic plants, benthic invertebrates, or aquatic emergent insects collected from the four sampling grids. For sediments, there was considerable variability due to limited sample number and heterogeneity of measured concentrations. Concentrations of PCBs in sediments and crayfish at the KRAOC were greatest at grid 4, but no statistically significant differences in PCB concentrations were observed among any of the grids within the KRAOC. Only one sediment sample was analyzed from grid 1 at the KRAOC; therefore the low concentration of total PCBs measured at this location (0.02 mg/kg wet weight) was likely an artifact of the low sample size and heterogeneity of PCB concentrations in the sediment. The lack of statistical differences within each of the two sites justified combining samples from different sampling grids on a site-specific basis for further analysis.

Temporal Variability in Total PCB Concentrations. At the KRAOC and FC, there were no significant differences in total PCB concentrations among sediments or invertebrates collected during different sampling periods in 2000. There was a trend toward decreasing concentrations of total PCBs in KRAOC sediments from spring to autumn sampling periods; however, these differences were not statistically significant. These results indicate that there are no seasonal effects during the spring and summer months in either organism behavior or PCB availability that play an important role in the concentrations of total PCBs accumulated among sediments or lower trophic level animals. The lack of statistical differences between sampling periods justified combining samples from different sampling periods on a site-specific basis for further analysis.

Spatial Variability in Total PCB Concentrations: KRAOC versus FC. Sediments, benthic invertebrates, aquatic emergent insects, crayfish, fish, muskrats, as well as tree swallow eggs and nestlings collected from the KRAOC had significantly greater concentrations of total PCBs when compared to those same matrices collected at the FC reference area. In general, a 1 order of magnitude difference in total PCB concentrations was observed among biota at the two locations (Table 1). However, PCB concentrations in sediments at the KRAOC were 2 orders of magnitude greater than sediment concentrations at FC (Table 1). Mink, adult tree swallows, and aquatic plants collected at the KRAOC did not have significantly greater total PCB concentrations compared to similar samples collected from the reference area. At the given sample sizes and observed variability, the concentrations for KRAOC samples needed to be approximately 2-, 6-, and 4-fold greater than concentrations at the FC for significant differences to be detected for mink, adult tree swallows, and aquatic plants respectively ($\alpha = 0.05$, $\beta = 0.20$). Unlike invertebrates or fish, plants do not appear to bioaccumulate PCBs to a great extent (19). The lack of a statistically significant difference in total concentrations of PCBs in adult tree swallows and mink between the KRAOC and the reference location is probably due to the life history and dietary composition of these animals. Adult tree swallows are migratory, so thus their overwintering exposures may contribute to their overall exposure to PCBs. Therefore, adult birds may be less indicative of local PCB concentrations (20). In addition, mink in this area feed on a variety of prey items that may have had relatively less PCB residue concentrations (such as muskrats). Also, the mink are likely feeding on prey from the terrestrial environmental or from tributary environments where PCB concentrations are less. It could also be that the dietary composition of mink may be different along the river. For example, one speculative explanation for the observed concentrations in mink liver could be that the upstream mink consume relatively more fish and the mink downstream consume more muskrat. This may have contributed to the lack of a significant difference in total PCB concentrations between the KRAOC and FC. Thus, assuming that mink (or

TABLE 1. Total PCB Concentrations (mg/kg) in Sediment (Dry Weight) and Aquatic-Associated Biota (Wet Weight) from the Former Trowbridge Impoundment (KRAOC) and the Fort Custer State Recreational Area Reference Site (FC)^a

	KRAOC location			FC location		
	N	mean % lipid ^b	total PCBs ^c	N	mean % lipid ^b	total PCBs ^c
sediments ^b	7	4.46	4.09 ± 4.40 (1.66) ^e	4	0.83	0.024 ± 0.005 (0.024)
aquatic plants	8	0.31	0.04 ± 0.03 (0.0249)	2	f	0.01 ± 0.00 (0.004)
benthic invertebrates (all orders including miscellaneous composites)	34	7.01	1.00 ± 0.79 (0.680) ^e	23	3.95	0.14 ± 0.06 (0.128)
molluska		f	f	1	2.75	0.20 (0.196)
plecoptera	3	4.60	1.60 ± 1.00 (1.43)	2	3.34	0.16 ± 0.10 (0.140)
trichoptera	1	10.9	1.17 (1.17)	4	4.34	0.17 ± 0.04 (0.164)
emphemeroptera	1	7.05	2.53 (2.53)	1	4.89	0.14 (0.144)
coleoptera		f	f	1	5.50	0.11 (0.114)
diptera		f	f	1	2.75	0.05 (0.048)
megaloptera	4	3.42	0.78 ± 0.30 (0.729) ^e	5	4.70	0.17 ± 0.04 (0.162)
isopoda	1	4.25	0.82 ± 0.00 (0.818)	1	7.10	0.10 (0.098)
neuroptera		f	f	1	3.36	0.15 (0.146)
odonata	5	2.36	0.20 ± 0.12 (0.184)		f	f
amphipoda (scuds)	4	5.26	1.76 ± 0.79 (1.57)		f	f
gnathobdellida (leeches)	1	2.36	0.73 (0.733)		f	f
aquatic emergent insects (all orders including miscellaneous composites)	33	7.50	0.74 ± 0.56 (0.569) ^e	16	6.42	0.13 ± 0.08 (0.104)
trichoptera	8	8.91	1.16 ± 0.45 (1.09) ^e	4	7.24	0.18 ± 0.05 (0.174)
diptera	9	8.31	0.45 ± 0.24 (0.406) ^e	4	3.85	0.04 ± 0.02 (0.035)
megaloptera	1	5.76	0.48 (0.481)	1	6.16	0.06 (0.061)
odonata	5	5.12	0.32 ± 0.22 (1.19)		f	f
ephemeroptera	2	4.15	1.89 ± 1.11 (1.72)	2	10.3	0.24 ± 0.06 (0.237)
plecoptera	2	7.85	0.41 ± 0.22 (0.380)		f	f
nematocera	1	7.44	1.03 (1.03)		f	f
crayfish	13	5.82	0.54 ± 0.53 (0.373) ^e	4	0.84	0.06 ± 0.03 (0.049)
fish ^d (all species)	20	3.70	4.35 ± 2.42 (3.59) ^e	21	4.82	0.86 ± 0.41 (0.795)
Northern hognose sucker		f	f	6	2.82	0.79 ± 0.07 (0.783)
forage fish	5	4.04	3.20 ± 1.30 (2.97) ^e	5	3.84	0.64 ± 0.21 (0.610)
golden redbreast sucker	4	6.32	4.60 ± 1.51 (4.39)		f	f
white sucker	1	0.75	0.42 (0.417)		f	f
carp	5	3.68	3.78 ± 2.28 (3.24) ^e	5	10.3	1.14 ± 0.74 (0.972)
smallmouth bass	5	1.90	6.67 ± 2.56 (6.26) ^e	5	2.70	0.89 ± 0.30 (0.861)
tree swallow adults ^d	9	6.46	8.67 ± 9.65 (4.90)	2	6.84	1.49 ± 0.65 (1.42)
tree swallow nestlings ^d	13	7.43	3.09 ± 1.61 (2.77) ^e	12	7.07	0.46 ± 0.51 (0.333)
tree swallow eggs	15	7.57	5.38 ± 4.30 (3.99) ^e	21	11.41	0.81 ± 0.54 (0.664)
muskrat ^D	7	2.44	0.07 ± 0.03 (0.0556) ^e	4	3.65	0.01 ± 0.01 (0.012)
mink liver	9	5.2	2.71 ± 1.96 (1.64)	3	3.40	2.27 ± 1.22 (2.09)

^a Combined data from all rounds and all years. ^b Mean percent organic carbon reported for sediments. ^c Total PCBs are presented as the arithmetic mean ± standard deviation (geometric mean). ^d Whole body. ^e Significant difference from the FC reference area at $p < 0.05$. ^f Data not available.

other organisms in general) eat only one species in their diet or that they feed in only one area can result in significant uncertainty regarding exposure to residues such as PCBs.

Concentrations of Lipid-Normalized Total PCBs in Aquatic Food Web Components. The relative concentrations of total PCBs were examined in the aquatic food web at the KRAOC and FC, including both mammalian and avian aquatic-based wildlife (e.g., mink and tree swallows). At both FC and the KRAOC, there was a general trend among biota toward greater concentrations of total PCBs at higher trophic levels (Table 1). Adult tree swallows and fish at the KRAOC, which occupy positions near the top of the food web, accumulated more PCBs than all other organisms.

At KRAOC, the rank order of lipid- or organic-carbon-normalized total PCB concentrations in the mink food web was: muskrat < aquatic plant < benthic invertebrates < crayfish ≤ mink liver < sediment < fish (Table 2). In the mink food web, only fish concentrations exceeded those of sediment. The rank order of lipid- or organic-carbon-normalized total PCB concentrations in the tree swallow food web at the KRAOC was: aquatic emergent insects < aquatic plant < benthic invertebrates < tree swallow nestlings < tree swallow eggs < sediments < tree swallow adults. Concentrations in only the highest measured trophic level

of the avian food web, adult tree swallow, exceeded the concentrations in sediment. All other lower trophic level biota in the avian food web had concentrations less than that found in the sediment.

At FC, the rank order of lipid- or organic-carbon-normalized total PCB concentrations in the mink food web was: muskrat < sediment < benthic invertebrates < crayfish < fish < mink liver (Table 2). The rank order of lipid- or organic-carbon-normalized total PCB concentrations in the tree swallow food web at FC was: sediments < benthic invertebrates < aquatic emergent insects < tree swallow nestlings < tree swallow eggs < tree swallow adults. It should be noted that 1 of the 16 aquatic emergent insect samples was omitted from the calculation of lipid-normalized total PCB concentrations due to an exceedingly low lipid concentration. If this single sample is included, then the lipid-normalized total PCB concentration for aquatic emergent insects at FC is 78.61 mg/kg. At FC, only muskrat exhibited concentrations less than that of the sediment. This is likely due to the herbivorous nature of muskrats. All other biota accumulated concentrations of PCBs greater than those measured in the sediment.

Biota-Sediment Accumulation Factors and Biomagnification Factors. The contrasting relationship between

TABLE 2. Concentrations of Lipid-Normalized Total PCBs (± 1 Standard Deviation) in Aquatic Food Web Components at Both the Kalamazoo River Area of Concern (KRAOC) and the Fort Custer State Recreational Area Reference Site (FC)

	KRAOC location		FC location	
	<i>N</i>	lipid-normalized total PCBs ^a (mg/kg, wet weight)	<i>N</i>	lipid-normalized total PCBs ^a (mg/kg, wet weight)
sediment (dry weight; organic-carbon-normalized)	7	105 \pm 113 (45.0)	4	3.74 \pm 2.33 (3.28)
aquatic plant	8	15.5 \pm 19.3 (8.62)	<i>b</i>	<i>b</i>
benthic invertebrates	33	29.1 \pm 26.9 (19.8)	22	4.10 \pm 1.61 (3.76)
aquatic emergent insects	33	11.81 \pm 16.95 (8.09)	16	4.88 \pm 11.0 (1.96)
crayfish	13	38.8 \pm 52.6 (19.3)	4	10.2 \pm 7.77 (7.78)
fish	20	174 \pm 171 (118)	21	23.4 \pm 12.4 (19.8)
tree swallow adults	9	157 \pm 149 (84.9)	2	21.6 \pm 8.47 (20.7)
tree swallow nestlings	13	46.5 \pm 21.4 (42.3)	12	6.83 \pm 5.26 (5.32)
tree swallow eggs	15	68.7 \pm 40.9 (57.0)	21	8.79 \pm 5.81 (6.80)
muskrat	7	3.01 \pm 1.43 (2.69)	4	0.644 \pm 0.556 (0.48)
mink liver	9	60.5 \pm 40.6 (34.6)	3	68.8 \pm 25.7 (64.9)

^a Individual samples were lipid-normalized prior to calculating the mean for a category. Total PCBs are presented as the arithmetic mean \pm standard deviation (geometric mean). ^b Not available.

TABLE 3. Bioaccumulation Factors of Total PCBs among the Aquatic Food Web at the Kalamazoo River Area of Concern (KRAOC) and the Fort Custer State Recreational Area Reference Site(FC)

trophic transfer	KRAOC location		FC location	
	lipid-normalized ^a	wet weight ^b	lipid-normalized ^a	wet weight ^b
Biota—Soil Accumulation Factor (BSAF)				
sediment \rightarrow aquatic plant	0.191	0.015	NA	0.189
sediment \rightarrow benthic invertebrate	0.439	0.409	1.15	5.44
sediment \rightarrow aquatic emergent insects	0.180	0.343	0.597 ^c	4.41
sediment \rightarrow crayfish	0.429	0.225	2.37	2.07
sediment \rightarrow fish	2.61	2.16	6.03	33.8
sediment \rightarrow tree swallow egg	1.27	2.40	2.07	28.2
sediment \rightarrow tree swallow nestling	0.939	1.67	1.62	14.2
sediment \rightarrow tree swallow adult	1.88	2.95	6.32	60.3
sediment \rightarrow muskrat	0.060	0.033	0.146	0.530
sediment \rightarrow mink	0.796	0.987	19.8	88.7
Biomagnification Factor (BMF)				
aquatic plant \rightarrow muskrat	0.31	2.23	NA	2.80
aquatic emergent insects \rightarrow tree swallow eggs	7.05	7.02	3.47	6.40
aquatic emergent insects \rightarrow tree swallow nestlings	5.23	4.87	2.71	3.21
aquatic emergent insects \rightarrow tree swallow adults	10.5	8.62	10.6	13.7
tree swallow adults \rightarrow tree swallow eggs	0.672	0.815	0.328	0.468
crayfish \rightarrow mink	1.792	4.39	8.35	42.8
fish \rightarrow mink	0.295	0.457	3.28	2.62
muskrat \rightarrow mink	12.85	29.5	136	167

^a Lipid-normalized biomagnification calculations represent the ratio of the geometric mean of the lipid-normalized wet weight biota total PCBs to the geometric mean of the organic-carbon-normalized dry weight sediment total PCBs for BSAFs or to the geometric mean of other lipid-normalized wet weight biota total PCBs for BMFs. ^b Wet weight biomagnification calculations represent the ratio of the geometric mean of the wet weight biota total PCBs to the geometric mean of the dry weight sediment total PCBs for BSAFs or to the geometric mean of other wet weight biota total PCBs for BMFs. ^c It should be noted that 1 of the 16 aquatic emergent insect samples was omitted from the calculation the BSAF due to an exceedingly low lipid concentration. If this single sample is included, then the BSAF is 0.890.

biota and sediment at FC and the KRAOC is better demonstrated by comparison of the biota–sediment accumulation factors (BSAFs). At both the KRAOC and FC, BSAFs and biomagnification factors (BMFs) were calculated for various trophic levels of the aquatic food web (Table 3). At FC, BSAF values were greater than the KRAOC BSAF values. The lesser BSAF values at the KRAOC indicate reduced bioavailability or other kinetic limitations to uptake by the biota.

Concentrations of total PCBs in aquatic plants from the KRAOC were less than concentrations in sediments. The BSAF for aquatic plants at the KRAOC on a wet weight basis was 0.15 (Table 3). Thus, bioavailability and uptake for these aquatic plants appear to be limited. The BSAF for aquatic and terrestrial plants has been reported to be in the range of 0.3–10 (19, 21, 22). It has been suggested that, with increasing concentrations of PCBs, BSAF values in plants decrease due to kinetic limitations in PCB accumulation in plants (21), and it is possible that this phenomenon is being

observed in the KRAOC plant samples. The BSAF value for FC on a wet weight basis was 0.19.

For benthic invertebrates and aquatic emergent insects at FC, lipid-normalized PCB BSAFs were 1.15 and 0.60, respectively (Table 3). At the KRAOC, benthic invertebrates and aquatic emergent insects had BSAF values of 0.44 and 0.18, respectively, indicating reduced bioavailability of PCBs bound to sediments in the KRAOC. In a similar evaluation of organisms inhabiting a PCB-contaminated site, the BSAF for aquatic emergent insects based on total PCB concentrations was determined to be 11 (23), a value that is considerably greater than the BSAF reported here for aquatic emergent insects (Table 3). The great variability in BSAF values among different field sites underscores the fact that the BSAF, a field-determined value, is site-specific and should, in general, not be extrapolated from other sites because of associated uncertainties.

At FC, the lipid-normalized BSAF for crayfish was 2.4 (Table 3). At the KRAOC, the lipid-normalized BSAF value for crayfish was 0.43, which was greater than the BSAF value aquatic emergent insects collected from this site (Table 3). This difference in PCB accumulation among the invertebrate community is likely due to the fact that crayfish are opportunistic feeders, eating aquatic plants and aquatic emergent insects, other invertebrates, detritus, and even dead fish. Thus, it is possible that crayfish have a greater probability of accumulating PCBs through their diets as compared to aquatic emergent insects and other benthic invertebrates occupying a lower trophic position. The results from this study differ from the results of a study conducted with Lake Erie invertebrates (24), in which mayflies contained greater concentrations of PCBs than crayfish. Different aquatic environments with different trophic dynamics and different available prey items for crayfish could explain these differences in site-specific PCB accumulations.

Fish collected from FC had a relatively high BSAF of 6.03. At the KRAOC, the BSAF value for fish was 2.61, which is slightly lower than other reported BSAFs for fish (range of 2.8–3.9) (25, 26).

At FC, low PCB sediment concentrations influenced the relatively high BSAF value of 20 calculated for mink. However, lipid-normalized concentrations of total PCBs in mink from the KRAOC were less than the organic-carbon-normalized concentrations measured in sediments and the lipid-normalized PCB concentrations in fish. This observation was likely due to the dietary composition of mink inhabiting the KRAOC. Site-specific dietary analyses conducted on the Kalamazoo River indicated that resident mink eat a diet that is composed of 72% mammals, 14% fish, and 14% crayfish (14). If mink were eating only fish from the KRAOC, then one might expect that the concentrations of total PCBs in mink liver would be greater than that of fish. However, since mammals made up a large part of the mink diet on the Kalamazoo River, it is likely that this resulted in observed concentrations of PCBs that were less than what would be expected if mink were primarily eating fish. BMFs for PCBs in mink were calculated based on trophic transfer from crayfish, fish, and muskrats (Table 3).

Tree swallow eggs, nestlings, and adults collected from FC had BSAF values that ranged from 1.6 to 6.3 (Table 3). At the KRAOC, tree swallow adults, nestlings, and eggs from the KRAOC had BSAFs ranging from 0.94 to 1.9 (Table 3). These BSAF values were less than those reported for tree swallows inhabiting Saginaw Bay, Michigan, where PCB BSAFs for tree swallow eggs and nestlings were reported to be in the range of 8.8–9.3 (23). Again, this variability in field-determined BSAFs indicates the important role of site-specific characteristics, such as availability of prey items and sediment organic carbon content, in determining PCB accumulation by biota. Because of the variability associated with field-measured BSAFs, widespread use of BSAF models that do not incorporate site-specific BSAFs, other than in first tier investigations, is not recommended (25).

PCB BMFs from the trophic transfer from aquatic emergent insects to tree swallows varied based on the stage of development of the tree swallow. Adult tree swallows accumulated the most PCBs via trophic transfer from aquatic emergent insects, followed by similar accumulation by tree swallow eggs and nestlings. The reduced BMF in nestlings compared to adults is likely due to growth dilution of PCBs in growing nestlings (27).

PCB Congener Composition in Aquatic Food Web Components. In this study, certain PCB congeners were consistently measured in all matrices (Figure 1). This finding supports the understanding that certain penta- and hexachlorinated biphenyls, such as PCBs 99, 118, 138, and 153, contribute a large proportion of the total PCB load in aquatic

organisms (28). In this study, as in other studies, congeners containing more chlorine atoms were generally enriched while less chlorinated congeners were generally not enriched in upper trophic levels (23, 28, Figure 1). For example, the percent contributions of coeluting PCB congeners 37, 41, and 42 (tri- and tetrachlorinated congeners) to total PCB concentrations in sediments and aquatic plants were 8.6% and 6.9%, respectively. This percentage was 4.2%, 4.4%, and 1.1% in aquatic emergent insects, fish, and muskrat, respectively. The percent contribution of more chlorinated congeners, such as PCBs 138, 158, and 153, was greater in higher trophic levels in the aquatic food web. For example, PCBs 138 and 158 comprised 3.7% of the total PCBs in sediments, 2.9% of the total PCBs in aquatic plants, 6.7% of the total PCBs in aquatic emergent insects, 11.8% of the total PCBs in adult tree swallows, and 25.7% of the total PCBs in mink. Both the position of vicinal hydrogens and the number and position of chlorines influence the metabolism of PCB congeners (28). PCB congeners with vicinal hydrogen atoms at meta and para positions are more easily metabolized. However, PCB congeners lacking vicinal hydrogens at meta–para or ortho–meta positions are not readily metabolized in biota and make up a greater percentage of the total PCBs at successively higher levels in the food chain, Figure 1 (28). The different PCB congener profiles observed in upper trophic positions, especially in mink, indicate that congener patterns are altered by environmental weathering and differential toxicokinetics (Figure 1).

Calculation of TCDD Equivalents and Relationship to Total PCBs. Concentrations of $TEQ_{WHO-avian}$ or $TEQ_{WHO-mammal}$ were calculated based on measured concentrations of non-ortho-substituted PCB congeners, including PCBs 77, 81, 126, and 169, and mono-ortho PCB congeners, including PCBs 105, 118, 156, 157, and 167. PCBs 114, 123, and 189 (mono-ortho congeners) were not detected in any of the samples analyzed in this data set. In some samples, PCB 105 coeluted with PCB 132, PCB 156 coeluted with PCBs 171 and 202, PCB 157 coeluted with PCB 200, and PCB 167 coeluted with PCB 128. When calculating concentrations of $TEQ_{WHO-avian}$ or $TEQ_{WHO-mammal}$, it was conservatively assumed that mono-ortho PCB congeners that coeluted with other congeners made up 100% of the coelution mixture. For most samples, the absolute difference in TEQ concentrations calculated with and without coeluting mono-ortho congeners was less than 5 ppt. Thus, concentrations of $TEQ_{WHO-avian}$ or $TEQ_{WHO-mammal}$ were conservatively calculated and, in some cases, overestimated for certain samples due to coelution of some congeners. Both mammalian and avian TEF values were used to calculate concentrations of $TEQ_{WHO-avian}$ or $TEQ_{WHO-mammal}$ in lower food web components of the aquatic food web, since both mammalian and avian receptors were considered in this analysis (17).

Concentrations of TEQs were plotted against concentrations of total PCBs to evaluate the potential to calculate TEQs based on total PCBs when congener-specific information is not available. When the analysis is restricted to individual sample types at individual sites, the correlation can be as good as $R^2 = 0.86$ for the relationship between fish $TEQ_{WHO-mammal}$ and total PCBs at the KRAOC or as poor as $R^2 = 0.15$ for the relationship between aquatic emergent insect $TEQ_{WHO-avian}$ and total PCBs at the KRAOC. However, the ability to predict TEQs from total PCBs would be most useful if it could be applied across organisms and locations. When organisms were grouped according to their food web but analyzed separately for location, the best correlation ($R^2 = 0.74$) was found for the mammalian food web at FC (Figure 2). The poorest correlation ($R^2 = 0.16$) was found for the mammalian food web at the KRAOC. The correlation is decreased when the data from both sites are combined for either the avian or the mammalian food web. Thus, on the

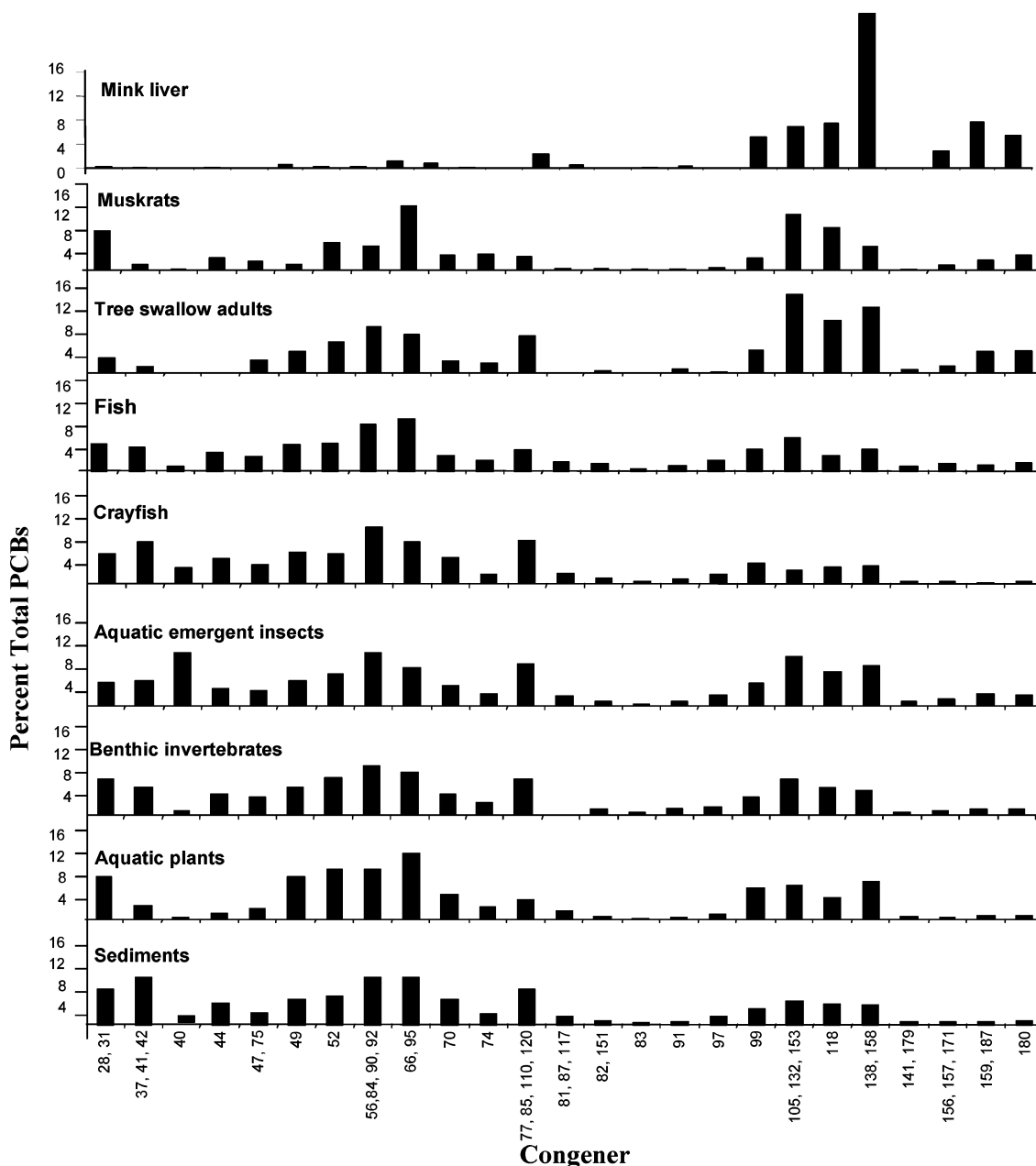


FIGURE 1. Mean concentrations of select PCB congeners in sediments, aquatic plants, benthic invertebrates, aquatic emergent insects, crayfish, fish, tree swallow adults, muskrats, and mink liver collected from the former Trowbridge impoundment.

basis of the extensive sample set and congener-specific analysis done at this site, it would be inappropriate to calculate TEQs from total PCBs at sites where congener-specific analysis was not conducted.

TCDD Equivalent Concentrations and Relative Potency in the Mammalian Food Web. Relative potency ($\mu\text{g TEQs/g PCBs}$), defined as the geometric mean of the $\text{TEQ}_{\text{WHO-avian}}$ or $\text{TEQ}_{\text{WHO-mammal}}$ concentration (ng/kg) divided by the geometric mean of the total PCB concentration (mg/kg) for that sample, was calculated for both mammalian and avian food webs. In the mammalian food web, mink were considered as the terminal trophic level organism while tree swallows were considered the terminal trophic level organisms in the avian food web.

In the mammalian food web at FC, $\text{TEQ}_{\text{WHO-mammal}}$ concentrations increased with trophic position. Sediment $\text{TEQ}_{\text{WHO-mammal}}$ concentrations at FC were less than $\text{TEQ}_{\text{WHO-mammal}}$ concentrations measured in all biota from the site, except crayfish (Table 4). The relative potency was

greatest in muskrats at FC ($60 \mu\text{g TEQ/g PCBs}$). Relative potency values for all other matrixes at FC ranged from $18.9 \mu\text{g TEQ}_{\text{WHO-mammal/g PCBs}}$ (fish) to $43.4 \mu\text{g TEQ}_{\text{WHO-mammal/g PCBs}}$ (mink).

At the KRAOC, $\text{TEQ}_{\text{WHO-mammal}}$ concentrations did not increase with every upward shift in trophic position (Table 4). At this location, $\text{TEQ}_{\text{WHO-mammal}}$ concentrations in sediments were greater than $\text{TEQ}_{\text{WHO-mammal}}$ concentrations in benthic invertebrates, muskrats, and crayfish, illustrating the reduced bioavailability of coplanar and mono-ortho PCB congeners to these organisms (Table 4, Froese et al. (23)). Fish and mink from the KRAOC had greater $\text{TEQ}_{\text{WHO-mammal}}$ concentrations than the KRAOC sediments, indicating that $\text{TEQ}_{\text{WHO-mammal}}$ contributing congeners (coplanar and mono-ortho congeners) were being accumulated and biomagnified up the food chain. The relative potency for mink was $93 \mu\text{g TEQ/g PCBs}$, which was greater than the relative potencies of all other food web components, most likely due to the biomagnification and retention of nonmetabolizing coplanar

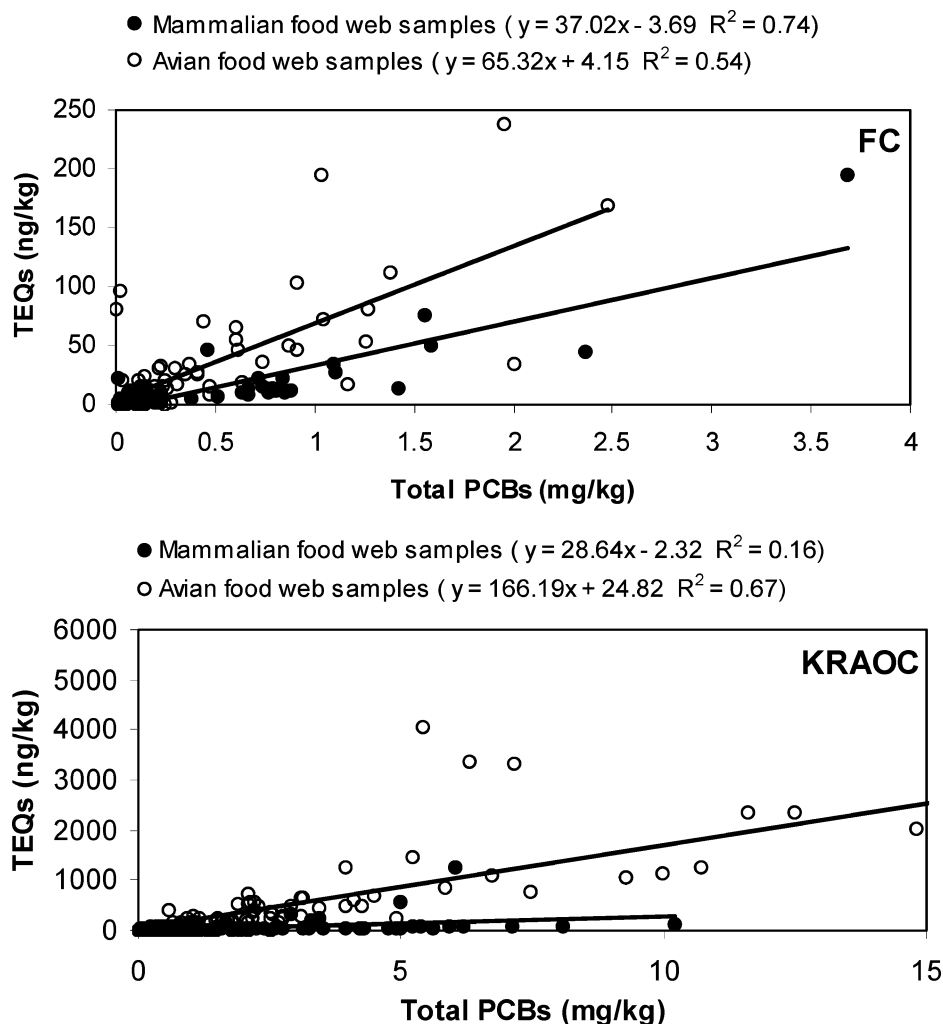


FIGURE 2. Relationship between total PCB and TEQ concentrations for the mammalian and avian food webs at the Fort Custer (FC) reference area and the Kalamazoo River Area of Concern (KRAOC). TEQs for items in the mammalian food web were calculated using WHO mammalian TEF values; likewise WHO avian TEF values were used to calculate TEQ for items in the avian food web. Mammalian food web items include sediment, benthic invertebrates, crayfish, fish, muskrat, and mink. Avian food web items include sediment, aquatic emergent insects, and tree swallow eggs, nestlings, and adults.

TABLE 4. Concentrations of $TEQ_{WHO-mammal}$ and Relative Potency Ratios among Various Trophic Levels in the Mammalian Food Web at Both the Kalamazoo River Area of Concern (KRAOC) and the Fort Custer State Recreational Area Reference Site (FC)

	KRAOC location			FC location		
	N	$TEQ_{WHO-mammal}^a$ (pg/g, wet weight)	biota/sediment relative potency ratio	N	$TEQ_{WHO-mammal}^a$ (pg/g, wet weight)	biota/sediment relative potency ratio
sediment (dry weight)	7	45.1 ± 53.2 (22.0)		4	2.29 ± 3.60 (0.972)	
benthic invertebrates	34	13.5 ± 8.47 (11.0)	1.2	23	4.40 ± 3.22 (3.39)	0.6
crayfish	13	6.71 ± 5.50 (5.21)	1.1	4	2.01 ± 1.27 (1.53)	0.8
fish	20	51.3 ± 26.7 (43.9)	0.9	21	17.6 ± 11.7 (15.0)	0.4
muskrat	7	1.37 ± 0.79 (1.10)	1.5	4	5.88 ± 11.2 (0.742)	1.4
mink	9	321 ± 395 (153.3)	6.5	3	107 ± 77.5 (90.4)	1.0

^a Concentrations of $TEQ_{WHO-mammal}$ were calculated using mammalian TEFs, and one-half of the MDL was used as a proxy value for congener concentrations that were below the MDL. Mono-ortho PCB congeners that coeluted were considered to make up 100% of the coelution mixture for TEQ calculations. Concentrations are presented as arithmetic mean \pm standard deviation (geometric mean).

and mono-ortho PCB congeners in mink. The relative potency of the KRAOC sediments was 13 μ g TEQ/g PCBs. Thus, the relative potency value of mink was approximately 7-fold greater than that of the KRAOC sediments (Table 4).

TCDD Equivalent Concentrations and Relative Potency in the Avian Food Web. TEQ concentrations for the aquatic food web were calculated based on the TEF_{WHO} avian values (17). TEQ potency differences in the sediment of the mammalian food web and aquatic food web are due to

different TEFs applied to the same PCB concentrations. In the avian food web at FC, $TEQ_{WHO-avian}$ concentrations in sediments were greater than $TEQ_{WHO-avian}$ concentrations in aquatic emergent insects, benthic invertebrates, and tree swallow nestlings (Table 5). However, the $TEQ_{WHO-avian}$ concentrations in egg and adult tree swallows were approximately 1.5 and 6 times greater, respectively, than $TEQ_{WHO-avian}$ concentrations in sediments (Table 5). Growth dilution and increased metabolic activity are likely explana-

TABLE 5. Concentrations of TEQ_{WHO-avian} and Relative Potency Ratios among Various Trophic Levels in the Avian Food Web at Both the Kalamazoo River Area of Concern (KRAOC) and the Fort Custer State Recreational Area Reference Site (FC)

	N	KRAOC		N	FC	
		TEQ _{WHO-avian} ^a (pg/g, wet weight)	biota/sediment relative potency ratio		TEQ _{WHO-avian} ^a (pg/g, wet weight)	biota/sediment relative potency ratio
sediment (dry weight)	7	606 ± 809 (307)		4	36.3 ± 70 (4.51)	
benthic invertebrates	34	103 ± 85.7 (63.6)	0.5	23	9.88 ± 7.85 (6.32)	0.3
aquatic emergent insects	33	87.3 ± 79.8 (57.1)	0.5	16	6.95 ± 4.62 (3.00)	0.2
tree swallow Egg	15	797 ± 668 (584)	0.8	21	55.8 ± 38.9 (43.3)	0.3
tree swallow nestling	13	597 ± 248 (556)	1.0	12	20.4 ± 13.1 (15.3)	0.2
tree swallow adult	9	2180 ± 1794 (1099)	1.2	2	216 ± 29.8 (215)	0.8

^a Concentrations of TEQ_{WHO-avian} were calculated using avian TEFs, and one-half of the MDL was used as a proxy value for congener concentrations that were below the MDL. Mono-ortho PCB congeners that coeluted were considered to make up 100% of the coelution mixture for TEQ calculations. Concentrations are presented as arithmetic mean ± standard deviation (geometric mean).

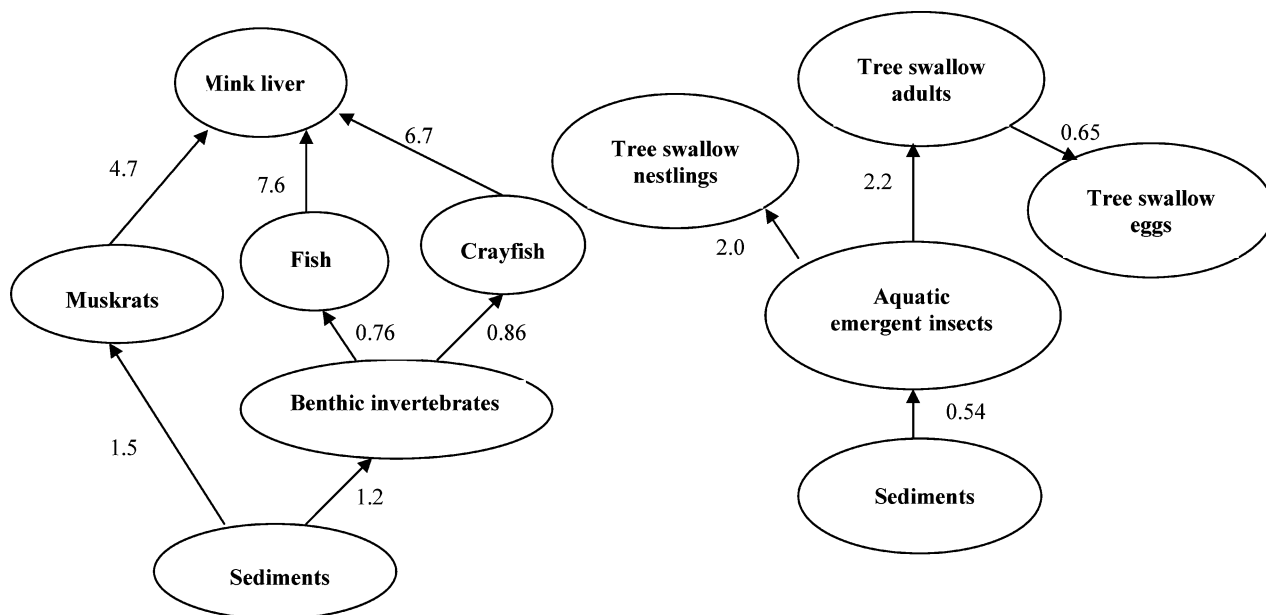


FIGURE 3. Ratios of relative potency among the mammalian and avian food webs at the Kalamazoo River Area of Concern (KRAOC).

tions for decreased TEQ_{WHO-avian} concentrations in FC nestlings as compared to egg and adult tree swallows. The relative potency was greatest in FC sediments (192 μ g TEQ/g PCBs), while lesser values were observed in FC biota (29–152 μ g TEQ/g PCBs).

At the KRAOC, TEQ_{WHO-avian} concentrations were greatest in tree swallow adults, followed by tree swallow eggs, sediments, and tree swallow nestlings (Table 5). The relative potency of the KRAOC sediments was 185 μ g TEQ/g PCBs. As in the mammalian food web at the KRAOC, the greatest relative potency value in the avian food web at the KRAOC corresponded with the highest avian trophic level studied, the adult tree swallow, which had a relative potency of 224 μ g TEQ/g PCBs. Thus, the relative potency in KRAOC tree swallow adults was approximately 1.2-fold greater than that of the KRAOC sediments (Table 5). The relative potency values of the KRAOC tree swallow eggs, nestlings, and adults were at least an order of magnitude greater than the relative potency values measured in merganser eggs collected near Green Bay, WI (29). Total TEQ_{WHO-avian} concentrations in tree swallow eggs collected from the KRAOC (797 pg/g, ww) were almost 3 times greater than TEQ_{WHO-avian} concentrations in merganser eggs collected from Lake Michigan (290 pg/g, ww). However, mean total PCB concentrations in tree swallow eggs from the KRAOC (5.38 mg/kg, ww) were an order of magnitude less than total PCB concentrations measured in merganser eggs collected from Lake Michigan (23.0 mg/kg, ww) (29).

Relative Potency Ratios. The ratio of the relative potencies between trophic levels indicates how the toxic potency of PCB mixtures changed from one trophic level to the next (Figure 3). In the mammalian food web at the KRAOC, an increase in relative potency values was observed in the trophic transfer from fish, crayfish, and muskrats to mink liver (Figure 3). This relatively great increase in relative potency was not observed in the avian food web at the KRAOC (Figure 3). Differential metabolism and other toxicokinetic differences between mink and tree swallows may explain the greater shift in relative potency values in the mink liver compared to that of the tree swallow. In addition, mink are at least one trophic position above that of tree swallows, and therefore a greater relative potency ratio in mink livers is to be expected (Figure 3). The results of this investigation illustrate that the concentration of total PCBs and toxicity of total PCBs, as indicated by TEQ concentrations, generally increase as trophic position increases.

Since the most toxic mode of action of PCBs on wildlife is mediated by coplanar and mono-ortho PCB congeners, which operate through the Ah receptor, TEQ_{WHO} concentrations in organisms, rather than total PCBs, are thought to be a more accurate representation of toxicity and risk toward wildlife. In this vein, the USEPA has issued a draft framework for the application of the TEQ methodology for dioxins, furans, and PCBs in ecological risk assessments (30). However, in a recent study by Custer et al. (31), TEQ concentrations based on PCB exposure did not accurately predict effects in

birds. Custer et al. (31) derived a LD₅₀ concentration of 1700 pg/g of TEQ_{WHO-avian} primarily due to TCDD exposure. In contrast, PCB-based concentrations of TEQ_{WHO-avian} between 1730 and 12700 pg/g ww caused only minimal effects on subtle endpoints in tree swallows from the Hudson River (32). As these bird studies indicate, the toxicity related to TCDD concentrations may not be equivalent to PCB-based TEQ_{WHO-avian} concentrations. Thus, increased research may be needed to refine avian TEF values for PCBs so that TEQ_{WHO} concentrations can more accurately predict toxic effects and be increasingly used in ecological risk assessments.

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Supporting Information Available

Congener-specific data for the Trowbridge and Fort Custer sites. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Supplemental Data Table for Fort Custer (Aquatic Food Web)

Type and Sample size (n)	Sediment (n=4)		Plants (n=2)		Benthic Inverts. (n=23)		Aq. Emerg. Insects (n=16)		Crayfish (n=4)		Fish (n=21)		Tree Swallow Adults (n=2)		Tree Swallow Nestlings (n=12)		Tree Swallow Eggs (n=21)		Muskrats (n=4)		Mink Liver (n=3)	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
Lipid or TOC (%)	0.828	0.454			3.95	1.62	6.42	4	0.842	0.515	4.82	3.31	6.84	0.332	7.07	3.31	11.4	6.67	3.65	3.9	3.4	1.28
Total PCBs (mg/kg)	0.0238	0.00479	0.00512	0.00359	0.142	0.0556	0.133	0.0813	0.0569	0.0341	0.859	0.412	1.49	0.651	0.456	0.51	0.815	0.533	0.0142	0.00872	2.27	1.22
Total PCBs (pg/g)	23800	4790	5120	3590	142000	55600	133000	81300	56900	34100	859000	412000	1490000	651000	456000	510000	815000	533000	14200	8720	2270000	1220000
PCB Congener																						
4, 10	INT		INT		INT		8330	11000	INT		9030	6780	INT		INT		1	0	INT		1	
5, 8	205	170	433		288	727	65.4	132	1	0	7840	3970	1000	1410	75.5	166	1	0	607	331	776	1100
6	9.81	16.8	1	0	4320	6400	1590	2360	1	0	5120	9300	1		1	0	1720	5620	598	706	1120	1170
9	43.7	73.3	INT		1690	2900	79.8	149	567	492	9810	29000	1		136	301	1	0	2230	788	1080	
15,17	1830	636	1670	2280	546	568	987	3160	4290	4550	16300	64700	111	156	4920	5160	1	0	3890	5490	1	
16,32	106	132	1		141	293	28.9	74	1	0	2620	3810	1	0	229	508	1	0	1	0	112	192
18	1.34	0.179	1	0	2410	8140	107	179	1	0	8820	14800	147	206	1	0	1	0	1	0	1	0
19	298		INT		407	812	10.1	36.5	2760	5360	18200	39000	1	0	460	1300	1	0	1040	2080	1	0
20,33,53	407	604	1	0	4430	7470	188	303	39.5	77	4040	4190	1	0	318	706	1170	3830	1	0	1	0
22	193	177	1		255	288	416	1300	16.8	31.6	1790	1960	1	0	155	288	4090	7810	1	0	1	0
25	40.7	31	246		1120	2700	1230	1680	10.6	19.3	61	275	1490		380	640	1	0	1	0	1700	2940
26	1.42	0.119	361		789	1360	149	235	46.3	78.5	5520	6240	153	215	683	1010	2880	8000	1950	834	908	417
27	1.34	0.179	INT		554	1080	252	955	1	0	1080	2030	1880	2650	13.1	40.1	1770	6760	1	0	1	0
28,31	411	191	1.5	0.707	3340	3470	1860	1170	1120	606	21900	31400	9430	530	4270	3380	4090	5660	440	330	2500	638
37,41,42	296	239	2	0	2610	2240	2030	3470	359	324	13400	10500	4380	480	4250	3610	4790	12400	2	0	1380	1280
40	146	138	1	0	405	382	155	173	1	0	2910	5210	447	630	46.1	150	3610	16500	1	0	1000	1740
44	818	374	INT		2240	1890	1410	1450	678	741	9330	6630	521	735	4110	4010	3240	6690	1	0	687	1190
45	485	404	88.9		188	273	142	240	1	0	3650	6220	2340	3020	121	304	3070	8280	1	0	1	0
47,75	170	124	1		5900	4820	1400	1350	203		6050	5180	3620	5110	4210	2940	9670	13800	1		1060	
49	428	122	98.8		2850	2220	2160	2240	979	942	13400	8840	8520	4210	6160	4010	8270	15200	1	0	582	511
52	360	269	138	193	4860	3680	3770	3880	2190	1170	23200	16300	16300	6360	9500	6350	18100	19600	1	0	634	1100
56,92,84,90,101,113	2090	366	221	306	13000	5490	13700	13200	5290	3340	65700	31800	120000	46300	33300	18000	95200	57500	5	0	8750	5890
66,95,96	967	340	96.5	135	6240	2940	4820	3810	1950	1440	26200	21100	29600	6930	12800	6810	22800	18200	1	0	12600	18700
70	634	142	120		2640	1620	3080	2900	1090	674	20100	8800	16700	23600	5750	3130	11300	8300	1500	85.4	481	831
74	1540	570	34.6	47.5	2420	1900	1280	1390	472	811	7010	3880	4510	6380	3370	4630	1610	5100	1	0	2040	3530
77, 85, 110, 120	1820	267	407	375	10700	5340	8420	7680	2240	1500	44300	22500	66200	28000	40900	33000	135000	339000	365	309	41100	30800
81,87,117	519	107	46.1	63.7	INT		4900	4340	1450	1070	20200	10600	INT		10300	5810	14800	13000	1.75	0.5	4860	4410
82, 151	334	75.4	82.5	115	1960	1110	1210	979	457	199	14700	13900	5680	757	3800	2450	5680	6460	2	0	2	0
83	168	46.6	1	0	740	599	389	586	351	606	1880	1010	172	241	1760	1900	1140	2480	1	0	1	0
91	152	40.2	1	0	957	760	821	816	30.5	59	8490	9250	6640	573	2740	1940	6400	6360	1	0	2860	2480
97	303	57.8	INT		2680	2360	2000	1540	868	712	15800	8330	2010	1080	5150	3350	4140	6010	1	0	1	0
99	773	274	323		4370	1970	3940	3500	1860	1200	43300	18000	36400	21700	10300	6290	30200	22700	1	0	30600	30000
105, 132, 153	1780	438	160	223	16500	8660	14500	9870	4350	3320	104000	46200	324000	152000	39300	15600	120000	72300	2000	1830	22900	17900
107	98.5	31.9	1	0	745	501	933	1080	580	479	20400	11300	11000	2290	2390	992	6080	6250	1	0	149	143
118	1110	215	287		8750	4620	9380	9630	3040	2320	36200	18700	120000	67700	20000	9250	54300	39100	710	657	101000	98400
119	520	478	1	0	181	179	161	214	565	690	2190	1290	1690	2390	5090	5590	501	2290	1	0	155	267
126, 129, 178	337	299	1		991	762	695	703	41	80	5660	4430	10700	1720	705	700	6970	5480	1	0	12500	8270
128, 167,185	279	145	1		3080	1660	6070	9130	1960	2430	18800	10200	46200	25000	7640	3140	20500	15500	30.3	54.5	29100	23300
133, 134	944	317	161		417	426	2190	6560	762	1520	6750	7630	4660	502	3910	2850	6590	8880	57	110	6150	3510
135, 144	178	122	9.8	12.4	1360	758	942	853	480	379	6950	5910	8460	721	3260	1610	7240	5480	1	0	1	0
136	37.2	45.2	1	0	194	244	200	218	24.3	46.5	3440	15800	444	626	802	760	396	1330	1	0	1	0
137,176	233	91.8	1	0	3260	1680	1160	1340	1080	1420	7300	5310	26400	8130	4160	2080	9980	8520	2	0	20600	21900
138,158	1680	596	452		12100	5210	12700	8370	5560	3860	58500	28800	276000	185000	34100	13200	96300	60200	729	637	643000	396000
141, 179	226	102	20.8	28	1270	1010	1460	1270	1340	1520	11700	7030	15400	2870	3730	1510	9290	6110	1.25	0.5	294	254
156, 171, 202,157,201	250	93	62.5	84.1	2560	1790	4310	6570	1140	1590	14400	8550	31700	13200	4300	3160	20500	20700	46.8	87.5	36900	17800
159, 187	298	129	INT		3150	2710	2880	2540	1610	1250	14800	8290	82700	30200	9310	3520	44400	26000	116	230	151000	107000
170	198	77.5	218	277	1320	916	1270	1070	194	152	10300	6560	28400	14400	4060	1640	15300	9960	89	176	120000	63300
174	175	66.8	INT		966	1030	2920	7380	1850	2670	6920	3980	11700	1130	2620	985	5700	3630	1	0	2300	2250
177	117	64.5	1	0	817	804	523	543	840	1020	5240	4200	11800	424	1980	763	9250	6310	1	0	17600	14200
180	504	356	12.1	15.7	3050	1730	3830	3070	1260	477	21700	11600	98400	40400	8520	2930	54500	37700	544	395	322000	111000
183	98.5	44.5	12.4	16.1	905	767	1410	1160	404	460	5700	3090	19800	5660	2790	1290	10800	7860	1	0	13400	10100
194	125	128	1	0	273	533	589	839	66	76.5	6920	5050	1	0	1330	570	6710	5080	64.3	74	51900	29700
195, 208	23.8	39.1	1	0	1170	2140	820	1250	13.7	25.5	390	393	4530	424	223	277	2290	2750	1	0	12000	4440
200	1.34	0.179	1	0	1	0	29	112	1	0	32600	23900	1	0	10.4	31.1	1	0	1	0	1	0
199	92.3	60.6	611	862	609	565	548	862	247	164	3930	2460	15500	2620	1500	767	9790	5420	40.8	79.5	119000	71100
205	1.34	0.179	5.14	5.85	1	0	1010	4020	498	995	1	0	4									

Supplemental Data Table for Fort Custer (Aquatic Food Web)

Type and Sample size (n)	Sediment (n=4)		Plants (n=2)		Benthic Inverts. (n=23)		Aq. Emerg. Insects (n=16)		Crayfish (n=4)		Fish (n=21)		Tree Swallow Adults (n=2)		Tree Swallow Nestlings (n=12)		Tree Swallow Eggs (n=21)		Muskrats (n=4)		Mink Liver (n=3)	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
Lipid or TOC (%)	0.828	0.454			3.95	1.62	6.42	4	0.842	0.515	4.82	3.31	6.84	0.332	7.07	3.31	11.4	6.67	3.65	3.9	3.4	1.28
Total PCBs (mg/kg)	0.0238	0.00479	0.00512	0.00359	0.142	0.0556	0.133	0.0813	0.0569	0.0341	0.859	0.412	1.49	0.651	0.456	0.51	0.815	0.533	0.0142	0.00872	2.27	1.22
Total PCBs (pg/g)	23800	4790	5120	3590	142000	55600	133000	81300	56900	34100	859000	412000	1490000	651000	456000	510000	815000	533000	14200	8720	2270000	1220000

(4) Units are expressed as pg/g on a wet weight basis for all biota samples and on a dry weight basis for soil samples (arithmetic mean and standard deviation are shown).
(5) Congeners 77, 81, 126, and 169 were separated from coeluting congeners and interferences by clean-up on a carbon impregnated silica gel column and then analyzed by GC-MS.
(6) Grouping of PCB congeners indicates that those congeners co-eluted in one or more samples. In some cases, due to slightly different co-elution patterns (usually in different matrices), some congener data were mathematically co-eluted (i.e., summed together) in order to present the data in one coherent table.

Supplemental Data Table for Trowbridge (Aquatic Food Web)

Type and Sample size (n)	Sediment (n=7)		Plants (n=8)		Benthic Inverts. (n=34)		Aq. Emerg. Insects (n=33)		Crayfish (n=13)		Fish (n=20)		Tree Swallow Adults (n=9)		Tree Swallow Nestlings (n=13)		Tree Swallow Eggs (n=15)		Muskrats (n=7)		Mink Liver (n=10)	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
Lipid or TOC (%)	4.46	2.78	0.313	0.257	7.01	11.3	7.5	2.47	5.82	13.9	3.7	2.24	6.46	3	7.43	3.21	7.57	2.72	2.44	1.41	5.2	15.6
Total PCBs (mg/kg)	4.09	4.4	0.0378	0.0291	0.997	0.791	0.742	0.561	0.536	0.535	4.35	2.42	8.67	9.65	3.09	1.61	5.38	4.3	0.0653	0.0324	2.71	1.96
Total PCBs (pg/g)	4090000	4400000	37800	29100	997000	791000	742000	561000	536000	535000	4350000	2420000	8670000	9650000	3090000	1610000	5380000	4300000	65300	32400	2710000	1960000
PCB Congener																						
4, 10	INT		154		INT		5210	10600	1	0	18500	15000	INT		INT	0	INT		INT		2010	
5, 8	5280	5670	205	285	2450	3920	1540	7340	24.5	59.8	11600	7730	558	428	461	665	72.3	276	1480	1840	292	418
6	2340	1680	38	58.1	9550	13200	916	1500	249	410	5820	12000	1660	1930	1	0	1680	4420	598	587	767	1420
9	377	429	129	137	762	1930	2020	5010	507	1120	4090	5560	1030	127	415	1170	1	0	856	1210	2090	3280
15,17	51800	42200	680	972	13300	10700	7690	11600	2190	2880	30200	21700	2950	2900	11100	9140	11300	15000	294		2980	8290
16,32	54700	56200	915	840	11100	10500	4270	8410	1440	1770	41500	30600	679	718	9180	7690	5170	6680	1	0	1780	2170
18	78000	104000	533	275	17900	19300	6500	10700	6120	6020	72000	42800	774	723	4840	5960	3050	4490	702	898	214	673
19	9400	11400	103	68.1	5080	6680	992	1380	44	107	8860	19300	325	394	795	1200	95.6	366	2.29	3.4	479	1080
20,33,53	62300	56400	934	1150	12500	10500	4670	8510	1350	1390	45000	27000	3980	3890	8830	3930	4550	12100	230	384	68.9	215
22	28900	26800	472	466	6240	5390	2420	3990	1510	945	26900	15800	222	290	4760	4610	8600	8820	166	341	133	417
25	10500	10800	195	257	8060	7210	3190	4270	1510	920	14500	18300	2110	1300	9680	7710	5670	5250	213	477	242	497
26	22100	20300	1110	922	8070	7300	4650	7060	5510	2520	53500	44500	1180	1210	9980	5980	11500	9900	1240	1720	1630	2200
27	7450	9510	223	245	2500	3290	592	1210	315	609	6330	4610	393	668	1820	1230	717	1090	163	396	186	366
28,31	253000	314000	1970	2100	62300	48900	32200	38000	42200	49200	217000	116000	274000	371000	185000	163000	246000	243000	5460	6220	5000	5160
37,41,42	373000	433000	2770	1830	48100	45700	24600	26700	13200	10200	193000	129000	105000	145000	138000	67200	159000	125000	774	898	1500	1660
40	45000	64500	999	1160	6650	5710	3420	4490	1910	3310	33300	21900	4780	4580	6120	5080	10400	7580	129	228	47.8	99.9
44	168000	193000	1700	1240	37400	33100	21000	22500	6620	5470	155000	85100	9790	12200	63800	27300	60800	46500	1640	1280	1410	1640
45	23300	25000	320	212	6370	6170	5520	12100	10.3	29.5	26600	16500	494	687	2080	1780	4150	8060	380	426	1	0
47,75	71000	67300	1260	1510	31400	26100	21100	20800	10600	5040	118000	65100	224000	338000	92600	50000	151000	120000	1200	2370	12900	11000
49	191000	214000	2070	1790	47700	42100	33000	34100	42700	55200	206000	107000	336000	536000	197000	156000	263000	240000	752	627	5330	6150
52	216000	241000	1940	1360	65000	58800	41400	38700	49400	61200	229000	120000	488000	649000	220000	163000	417000	333000	3870	2330	4020	4340
56,92,84,90,101,113	358000	388000	3710	3340	87500	79200	65000	54500	49700	49800	378000	215000	737000	1010000	288000	127000	478000	401000	3290	2220	28400	31900
66,95,96	366000	412000	2760	2270	74600	57800	47200	40300	65200	83500	417000	227000	609000	884000	240000	120000	425000	345000	8840	5180	18500	22400
70	196000	222000	1760	1420	35400	31600	26400	27200	25000	40500	129000	69900	179000	249000	108000	59000	167000	128000	2030	1110	2490	4550
74	87200	113000	640	617	21500	15800	15300	11700	12200	13700	83100	55300	158000	233000	73400	42400	110000	103000	2150	1990	835	1720
77, 85, 110, 120	274000	312000	2880	2210	63500	61600	53600	40400	19600	24700	169000	86900	809000	874000	275000	146000	1720000	2250000	1880	1050	56600	54700
81,87,117	58800	61500	721	653	INT		15800	18400	8340	5190	75600	55700	89700	96200	70300	36600	122000	77400	340	361	10200	11800
82, 151	33400	38900	364	358	9120	7880	6080	4640	2680	2190	61800	50400	28100	26300	21500	8270	29700	21900	252	241	237	320
83	13900	14100	146	103	3660	2910	2520	2320	1120	626	18200	14300	2560	1290	7190	3160	14500	13900	71.4	130	2560	3560
91	20500	22900	297	309	11600	28500	5060	4230	5300	1880	44600	28400	64300	97600	24600	13200	31900	24600	90.7	158	6940	10200
97	71800	83300	622	689	14700	13900	12100	10300	2210	3340	84000	52100	16400	19000	51000	22500	52100	38100	441	457	215	468
99	120000	136000	1380	1240	31900	26100	27800	21600	31300	37900	175000	109000	368000	563000	119000	60000	233000	218000	1680	1140	124000	95900
105, 132, 153	181000	200000	899	695	62700	52600	65700	40200	33900	38000	269000	134000	1170000	1140000	251000	133000	571000	444000	7690	3670	168000	419000
107	14400	14600	56.5	68.4	4810	3560	4810	2960	2030	1260	74800	48000	68800	60900	19500	9920	35600	27600	304	246	731	1330
118	163000	178000	1120	1220	48500	39800	44300	28900	21500	14200	127000	67400	782000	832000	182000	81600	405000	353000	5850	3470	182000	156000
119	6020	6420	3.4	4.45	1870	1760	3320	5370	832	1030	16600	11700	22400	25900	6550	6210	13900	12900	466	553	1280	1340
126, 129, 178	5790	7150	35.9	65.1	3310	2900	2740	1600	438	433	20800	18400	23600	14200	5030	2170	16000	12300	272	200	23500	29300
128, 167,185	26300	31500	250	356	7830	7270	10500	9740	2580	1980	64800	55300	143000	109000	31200	13700	67200	48400	591	398	66200	69900
133, 134	22100	22600	734	898	2120	1870	2680	3040	1640	1600	21300	24100	20400	16600	10700	4370	20400	18100	231	175	10000	10000
135, 144	18200	21900	99.8	106	4700	4430	3900	2420	1940	1350	27600	27500	34400	32000	14600	8030	21200	15200	53.6	139	353	669
136	10700	13000	70	81.5	1630	1820	1070	842	195	288	5600	25000	3950	3320	3460	1140	3250	2740	15.7	38.9	1	0
137,176	16700	20600	75.6	81.2	7970	7150	5850	4950	2150	2050	22200	19300	81300	67100	19500	8980	37700	26900	274	375	27600	45100
138,158	156000	187000	1170	1170	44200	44300	47000	31100	36800	44700	174000	120000	962000	927000	196000	118000	420000	330000	3250	1730	628000	540000
141, 179	22500	26300	150	135	5210	6030	4560	3140	2730	2060	36800	30900	46900	47300	15300	7340	27700	20500	161	209	857	871
156, 171, 202,157,201	24100	30100	142	153	7780	8810	7950	8170	1930	1680	54800	46200	111000	79600	17200	9160	41800	30600	674	475	68900	64300
159, 187	26500	30700	85.7	92.6	10400	8700	13500	9520	3730	1970	50500	42100	316000	272000	45100	16600	129000	122000	1340	905	185000	209000
170	23200	24600	134	136	4120	3450	5600	3060	1330	1030	35200	33200	113000	99000	16300	8210	37700	28800	773	449	110000	86800
174	15100	17900	231	314	2970	3570	4680	7590	1820	1390	25400	24000	34800	33700	13100	12300	18900	13800	69.1	180	657	848
177	9340	12800	77.5	105	2830	2820	3270	3550	1260	805	21100	20200	47600	33100	8470	4020	21400	16900	324	277	50900	64400
180	32500	38100	137	120	9680	9660	15000	10500	393													

Supplemental Data Table for Trowbridge (Aquatic Food Web)

Type and Sample size (n)	Sediment (n=7)		Plants (n=8)		Benthic Inverts. (n=34)		Aq. Emerg. Insects (n=33)		Crayfish (n=13)		Fish (n=20)		Tree Swallow Adults (n=9)		Tree Swallow Nestlings (n=13)		Tree Swallow Eggs (n=15)		Muskrats (n=7)		Mink Liver (n=10)	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
Lipid or TOC (%)	4.46	2.78	0.313	0.257	7.01	11.3	7.5	2.47	5.82	13.9	3.7	2.24	6.46	3	7.43	3.21	7.57	2.72	2.44	1.41	5.2	15.6
Total PCBs (mg/kg)	4.09	4.4	0.0378	0.0291	0.997	0.791	0.742	0.561	0.536	0.535	4.35	2.42	8.67	9.65	3.09	1.61	5.38	4.3	0.0653	0.0324	2.71	1.96
Total PCBs (pg/g)	4090000	4400000	37800	29100	997000	791000	742000	561000	536000	535000	4350000	2420000	8670000	9650000	3090000	1610000	5380000	4300000	65300	32400	2710000	1960000

(4) Units are expressed as pg/g on a wet weight basis for all biota samples and on a dry weight basis for soil samples (arithmetic mean and standard deviation are shown).

(5) Congeners 77, 81, 126, and 169 were separated from coeluting congeners and interferences by clean-up on a carbon impregnated silica gel column and then analyzed by GC-MS.

(6) Grouping of PCB congeners indicates that those congeners co-eluted in one or more samples. In some cases, due to slightly different co-elution patterns (usually in different matrices), some congener data were mathematically co-eluted (i.e., summed together) in order to present the data in one coherent table.